

Thermophysical Properties of Methane: Virial Coefficients, Vapor and Melting Pressures*

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For use in the computation of thermodynamic properties in gaseous and liquid states at $T < 300$ K there are given concise descriptions of the properties named in the title. Numerous published data on methane are combined with some new analytical expressions which give more acceptable behavior than previously could have been achieved.

Key words: Melting pressures; methane; thermophysical properties; vapor pressures; virial coefficients.

List of Symbols

Subscripts c and t refer to critical and triple points.

$a, b, c, d,$	coefficients for eq (4).
$A, B,$	coefficients for eq (6).
$B_i, C_i,$	coefficients for eqs (2, 3).
$B(\tau), C(\tau),$	the "virial coefficients."
$d,$	density
$\Delta,$	any relative deviation, $(y/y_{\text{calc}} - 1)$.
$\epsilon,$	exponent in various expressions.
$J,$	the Joule.
$l,$	the liter.
mol,	16.042 g of methane.
$P,$	pressure, 1 atm = 0.101325 MN/m ² .
$R,$	the gas constant, 8.3143 J/(mol K).
$\sigma,$	d/d_c , density reduced at d_c .
$T,$	temperature, K on the IPTS (1968).
$\tau,$	T/T_c , temperature reduced at T_c .
$v,$	$1/d$, molal volume.
$x,$	defined argument in various equations.
$Y,$	dependent variable in eq (6).
$Z,$	Pv/RT , the "compressibility factor."

1. Introduction

It appears likely that many technological processes will increasingly involve the liquefaction, storage, and pumping of methane either as a pure fluid or as the major component of liquefied natural gas. Hence our ultimate objective is the determination of accurate thermodynamic properties for this fluid from room temperature down to the solid-liquid boundary, with

emphasis on the saturated and compressed liquid states.

Analytical description of physical properties is a practical necessity for the tedious computations which must be performed to obtain a network of thermodynamic functions. In the present report we select some published properties data and place them in analytical form directly useful for thermal computations. This work is appropriate because more data are available for methane than for any fluid previously studied experimentally at this laboratory. Data from different sources on a given property seldom are completely consistent. With the increase of available data we often suffer a decrease of precision. Our new analytical descriptions, however, are powerful tools for examining raw data because they are constrained to accepted fluids behavior, especially at the critical point [1, 2]¹. Their use provides a principal justification for reexamining data on methane.

Our particular objective in this and a following report is to describe the coexistence regions, because they are boundaries for PVT behavior in the one-phase domain. The virial equation of state (valid at densities below one half the critical density) is treated first, however, because it will be used to estimate some coexistence data. It also provides low-density PVT "data" not available through our high-density experimental techniques.

Temperatures in this report have been converted from the 1948 to the 1968 IPTS [3] via an interpolation program provided by Rolf Prydz.

The values of fixed-point constants selected for present work are given on the first two lines of table 1. Temperatures are on the IPTS–1968. In a following

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¹ Figures in brackets indicate the literature references at the end of this paper.

report on the orthobaric densities we had found $T_c = 190.5 \pm 0.1$ K. We then discovered two new investigations of the critical region [24, 25]. Values from these publications are given on the last two lines of table 1. Temperatures have been increased by 0.032 K to bring them onto IPTS-1968. To avoid proliferation of published critical-point constants we have adopted $T_c = 190.53$ K from [25]. Our critical-point pressure is given by the vapor pressure equation of the present report. Our critical-point density is obtained from our rectilinear diameter.

TABLE 1. Fixed-point constants for methane

Fixed point	T	P	d
	K	atm	mol/l
Triple point	90.66 [11]	0.1151	28.0536*
Critical point	190.53	45.346	10.15
C.P. [24]	190.58 ± 0.05	10.35 ± 0.13
C.P. [25]	190.530	45.346	10.1475

*Density of liquid at T_t .

2. The Virial Coefficients

It is convenient for correlation in corresponding states to define reduced variables $\tau \equiv T/T_c$, $\sigma \equiv d/d_c$. The truncated virial equation used here then is

$$Z = 1 + B(\tau) \cdot \sigma + C(\tau) \cdot \sigma^2. \quad (1)$$

The second and third virial coefficients $B(\tau)$, $C(\tau)$ are dimensionless.

Data for $B(\tau)$ have been selected from four sources [4, 5, 6, 7]. Representation of these data, needed for computations, is given by the same type of expansion as was used for hydrogen [8],

$$B(\tau) = \sum_{i=1}^6 B_i \cdot (1/\tau)^{(2i-1)/4}. \quad (2)$$

Data were eliminated, however, if they diverged more than 1 percent. We are left with the set of points plotted on figure 1. The line is calculated from (2) with coefficients

$$\begin{aligned} B_1 &= 16.67\ 707, & B_4 &= -203.22\ 428, \\ B_2 &= -87.41\ 490, & B_5 &= 108.55\ 0470, \\ B_3 &= 187.43\ 954, & B_6 &= -23.21\ 3116. \end{aligned}$$

The rms relative deviation for 25 points is 0.31 percent. Individual deviations, $\Delta \equiv (B/B_{\text{calc}} - 1)$, are given in percent on figure 2. Equation (2) may not be accurate for $\tau \geq 2$ with above coefficients.

Calculated data for $B(\tau)$ will be published by Sengers, Klein, and Gallagher using an intermolecular potential function adjusted to the experimental data

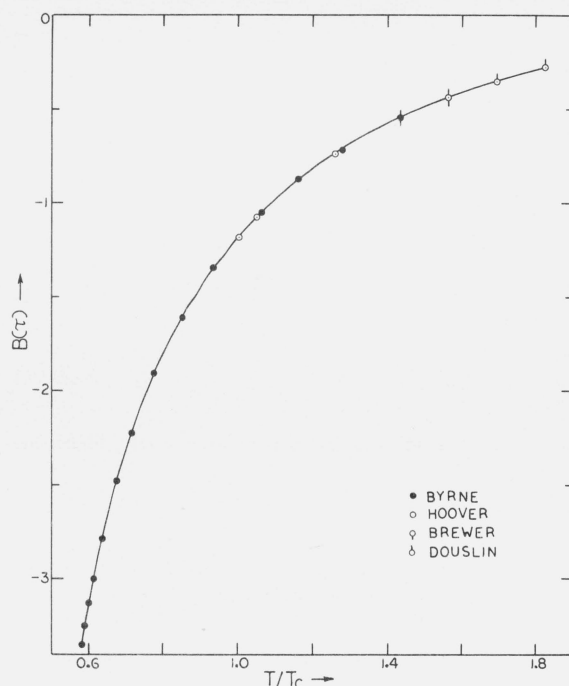


FIGURE 1. Second virial coefficient $B(\tau)$ for methane.

These data are represented by eq (2).

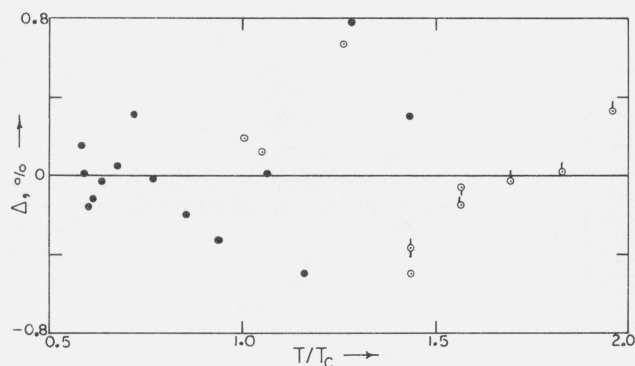


FIGURE 2. Relative deviations of second virial coefficient data from eq (2).

Points are identified as on figure 1.

[26]. For thermal computations this has the very important advantage that the temperature dependence is theoretically based, as compared with a polynomial adjusted to imprecise experimental data only. To see how drastic this may be, compare coefficients of eq (2) given above with values given below for data of [26] in the range $110 \leq T \leq 450$ K,

$$\begin{aligned} B_1 &= 2.109\ 914, & B_4 &= -16.022\ 404, \\ B_2 &= -7.268\ 397, & B_5 &= 9.450\ 4285, \\ B_3 &= 13.088\ 869, & B_6 &= -2.532\ 2231. \end{aligned}$$

The rms relative deviation for 47 data is 0.051 percent. There is no clear indication that the deviations are systematic. At $T \leq 200$ K no deviation exceeds 0.02

percent. At $T > 200$ K no deviation exceeds 0.17 percent.

For $C(\tau)$ few data are available at low temperatures. Figure 3 gives data of [5] at $\tau < 1.5$, and data of [7] at $\tau > 1.5$. We had devised a form for describing data on hydrogen [8], which later was modified [9], and now is further changed to obtain a better representation of these methane data,

$$C(\tau) = [C_1/\tau^{1/2} + C_2/\tau^5] \cdot [1 - \exp(1 - C_3 \cdot \tau^2)]. \quad (3)$$

The line on figure 3 is calculated from (3) with constants,

$$C_1 = 0.23844, \quad C_2 = 0.56243, \quad C_3 = 1.90.$$

The behavior given by (3) is quite similar to that of recent precise data on oxygen [10] for which a maximum value of $C(\tau) = 0.50$ occurs at $\tau = 0.9$. The root for oxygen is near $\tau_0 = 0.70$, whereas C_3 was selected for methane to shift this root to a slightly higher value.

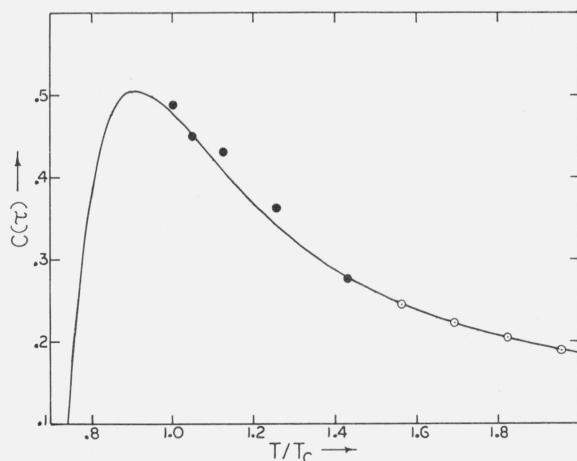


FIGURE 3. Third virial coefficient $C(\tau)$ for methane.

At $T/T_c < 1.5$, the data are from [5]; above 1.5 they are from [7]. The line is calculated with eq (3).

3. The Vapor Pressures

The vapor pressures of liquid methane have been observed by numerous authors, giving roughly 200 P - T pairs [11, . . . , 16]. Some data differ by several percent from the smoothed behavior of all data. Only by use of a reliable form of vapor-pressure equation with a minimum of arbitrary constants does it appear possible to attack this mass of data with relative confidence [1]. Our independent variable is

$$x(T) \equiv (1 - T_c/T)/(1 - T_c/T_c)$$

and the new equation is

$$\log_e (P/P_t) = a \cdot x + b \cdot x^2 + c \cdot x^3 + d \cdot x \cdot (1 - x)^\epsilon.$$

(4)

Exponent ϵ has been established at this laboratory through examination of more precise data on other substances: $\epsilon = 1.433$ for fluorine [17] and $\epsilon = 1.45 \pm 0.05$ for oxygen (Rolf Prydz); and $\epsilon = 1.45$ for nitrogen [27].

We take $\epsilon = 1.45$ for methane. At first we allowed the triple-point pressure in (4) to appear on the right as a least-squares coefficient, finding a value in agreement with [11], table 1. Thereafter we used (4) as written, constrained to the triple point. By use of (4) as a reliable smoothing function we successively eliminated inconsistent data, ending with 161 points and an rms relative deviation of 0.27 percent by use of coefficients,

$$a = 4.470 \ 3915, \quad c = -0.744 \ 4619,$$

$$b = 2.250 \ 3526, \quad d = 1.601 \ 7258.$$

Deviations are plotted on figure 4. Filled circles are 47 smoothed data recommended by Armstrong [11]. The remaining 114 points (N pts) and their ranges are

Author	N pts	Range, T , K
Bloomer [15]	17	111.4 – 190.4
Grigor [16]	32	98.2 – 188.9
Hestermans [14]	16	117.3 – 189.6
Itterbeek [12]	20	149.8 – 190.3
Vennix [13]	29	133.7 – 190.2

4. The Melting Pressures

Melting pressures $P(T)$ for coexisting solid and liquid methane have been observed to $P = 156$ [18] and in the range $970 \leq P \leq 2700$ atm [19]. Another three points at $P < 46$ [20] agree well with [18]. The latter authors gave methane vapor pressures at their melting temperatures. We have used temperatures derived from these vapor pressures via (4). They are at most 0.03 K higher than those given in [18].

To examine the melting pressures we plot $Y(P, T) \equiv (P - P_t)/(T - T_t)$ versus $x \equiv T/T_t$ as recommended in [21], figure 5. Solidly filled circles represent data from [19] used with triple-point constants of table 1.

For the data of [18] alone, the Simon melting equation

$$(P - P_t) = P_0 \cdot (x^\epsilon - 1) \quad (5)$$

yields an exponent ϵ in excess of 3.0, much greater than found for many other fluids [21]. The authors [19] found $\epsilon = 1.01$ and rounded the triple-point temperature to $T_t = 89$ K, making three adjusted constants. It is possible that their methane was insufficiently pure for present purposes. By adding 2 K to all of their temperatures, the points of figure 5 move down and to the right (large, open circles).

We now examine for comparison a possibly similar substance, argon, for which precise, independent data are available: from [22] to $P = 1500$; and from [23] at $970 \leq P \leq 6000$ atm. Figure 6 gives these argon data in the same range covered by the methane data. The

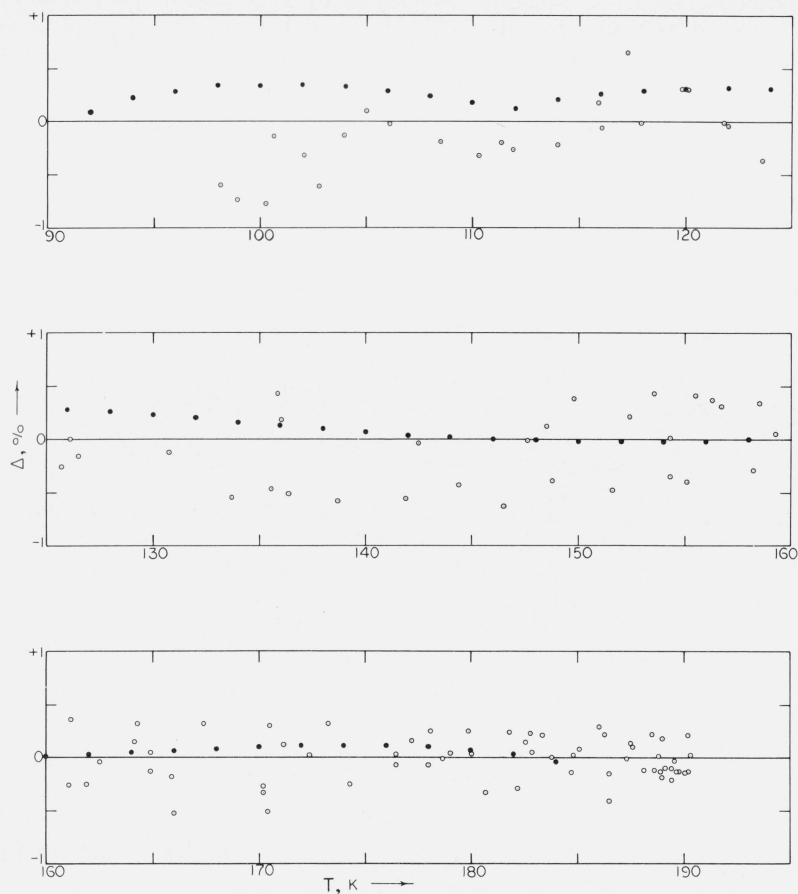


FIGURE 4. Relative deviations of methane vapor pressures from eq (4).

Filled circles are from [11].

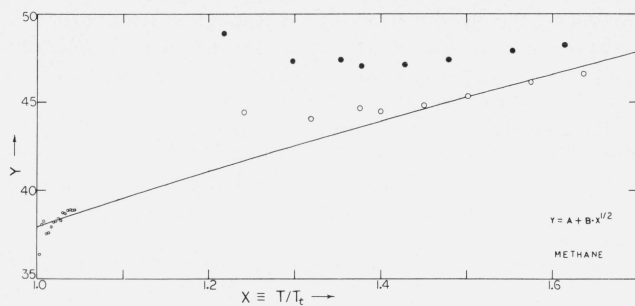


FIGURE 5. The melting function $Y \equiv (P - P_t)/(T - T_t)$ for methane.

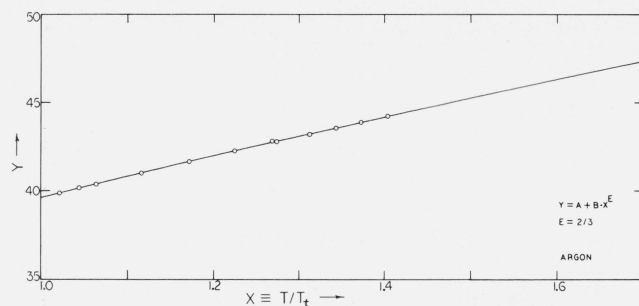


FIGURE 6. The melting function $Y \equiv (P - P_t)/(T - T_t)$ for argon.

16 argon pressures are represented with an rms relative deviation of 0.091 percent by the expression

$$Y(P, T) = A + B \cdot x^\epsilon, \quad (6)$$

$$A = 21.4192, \quad B = 18.1926, \quad \epsilon = 2/3,$$

which was used to draw the line on figure 6.

For methane on figure 5 we see that a greater curvature at the origin (than used for argon) should give a better representation. We arbitrarily take $\epsilon = 1/2$, to

give the provisional melting pressure equation (6) for methane with constants

$$A = 5.318, \quad B = 32.635, \quad \epsilon = 1/2$$

The line on figure 5 was calculated with these constants.

Melting pressures beyond our present range of interest have been observed to 24,000 atm [28]. To complete our reporting, however, we give these data on figure 7.

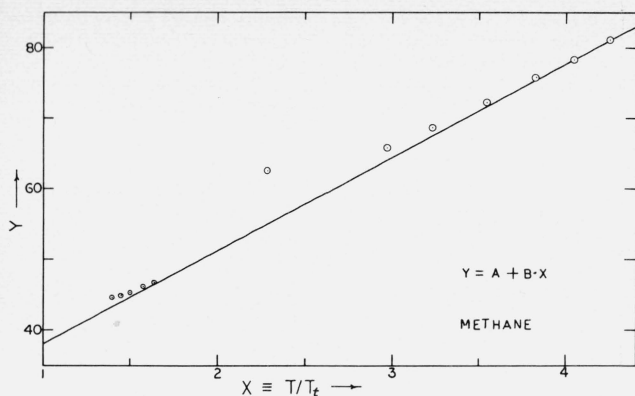


FIGURE 7. The melting function $Y \equiv (P - P_t)/(T - T_t)$ for methane up to $P = 24,000$ atm.

Small circles are from [19]; large circles from [28]. The line is $Y = 24.75 + 13.25 \cdot x$.

5. Conclusions

This correlation has been undertaken to evaluate the quality of existing physical properties measurements on compressed gaseous and liquid methane, to reveal significant gaps or inconsistencies in existing measurements, and to provide accurate analytical representations of selected data for preliminary thermodynamic computations. Selected data for the second virial coefficient at temperatures down to the normal boiling point are of good quality, but few if any consistent data exist for lower temperatures. Further results for the third virial coefficient are needed at low temperatures. For the vapor pressures, the rms deviation of 0.3 percent found here could be reduced one order of magnitude through self-consistent measurements of high accuracy [17]. New determinations of the melting pressures to about 300 atm clearly are needed. Available analytical expressions are capable of representing all of the properties we have examined within the precision of the measurements.

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